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Review of the *T*-history method to determine thermophysical properties of phase change materials (PCM)

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A B S T R A C T

Phase change materials (PCM) are able to store thermal energy when becoming liquid and to release it when solidifying. Latent heat storage has gained importance due the applications towards increasing energy efficiency in several systems. Thus, a correct and accurate thermal characterization of these materials should be achieved. Among all possible thermal analysis methods to determine PCM thermophysical properties, the *T*-history method presents certain advantages. The *T*-history method is known to be suitable to obtain fusion enthalpy, specific heat and thermal conductivity for large phase change materials samples. On the other hand, no experimental *T*-history equipment is commercially available yet. Therefore, the goal of this paper is moving towards a consensus. To achieve this goal, a collection of similar methods previous to *T*-history are exposed and different proposals based on improving the original *T*-history method are discussed and reviewed.

Contents

1. Introduction

Thermal energy storage (TES) systems are one of the most powerful alternatives in order to improve buildings energy efficiency. The materials which allow to store thermal energy are being widely studied by the international scientist community [1–3]. TES presents phase change materials (PCM) as an option to increase the thermal mass of the building envelopes and building

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Nomenclature

T	temperature (°C)
H	enthalpy (J g^{-1})
Cp	Specific heat at constant pressure (J g^{-1} °C^{-1})
T	time (s)
K	thermal conductivity (W m^{-1} K^{-1})
A_c	Convective heat-transfer area of a tube (m^2)
h	Natural convective heat-transfer coefficient of air outside a tube (W m^{-2} K^{-1})
q	heat loss (W)
Bi	Biot number
c	heat loss coefficients
m	Mass (g)

Subscripts

M	melting
T	tube
W	water, reference
P	PCM
L	liquid
Sn	sensor
s	solid
o	initial
r	end
∞	ambient air
i	points in temperature–time curves

systems by the latent heat produced during the phase change [4–6]. Furthermore, PCM have been recognized as one of the most advanced energy materials/technology in enhancing the energy efficiency and sustainability of buildings [7] and other application as stabilization of human temperature when working in extreme environment [8], in space industry [9], electronic industry, car industry [10], as well as for cold storage [11], solar cooling and concentration of solar energy in power plants [12,13], seasonal storage, etc.

Among all materials, those that have high storage density for small temperature range are considered PCM [14]. PCM are classified in different groups depending on the material nature. Cabeza et al. [15] proposed a classification divided into several groups based on PCM nature: salt hydrates, paraffin, fatty acids, etc.

During last years, it has been seen that PCM thermal characterization is a key factor when designing proper final constructive systems. Conventionally, thermal characterization of materials is performed using thermal analysis techniques [16,17]. Within these techniques, differential scanning calorimetry (DSC) is the widest used [18–20]. This is one of the most powerful techniques to thermophysically analyze a PCM because it provides the melting/solidification enthalpies, the melting/solidification temperatures and the specific heat of the materials under study. However, it presents some limitations: the small sample amount (less than 90 mg), the sample mass influence on the thermal response [18], the response dependence on the used heating rate [21], repeatability may not be reached when analyzing heterogeneous samples and, in the case of composite materials, the main component can interfere in the PCM DSC signal [22], etc. This is the reason why, other methods are being developed to analyze PCM in order to determine the heat of fusion and the specific heat capacity, both as a function of temperature.

The original *T*-history method was proposed by Yinping in 1999 [23]. This method is based on recording temperature versus time curves of the PCM and a well-known reference, usually water. Mainly, heat capacity, fusion and solidification enthalpies and phase change temperatures are determined using the *T*-history method. The invention of this new method was revolutionary in the field of thermal analysis, especially for PCM. The *T*-history method fulfilled the researchers' necessity to characterize PCM samples being the results more reliable and more faithful to the real thermal behavior obtained in building envelopes.

Many researchers are already using the *T*-history method to analyze PCM. Chiu and Martin [24] analyzed a salt hydrate and paraffin from Climator with the *T*-history method. Stankovic and Kyriacou [25] show temperature measurement results of RT21 comparing two different linearization techniques. Furthermore, Li et al. [26] state that the maximum deviation between *T*-history measurements and the values from DSC and references is less than 8%, states, when evaluating eutectic mixture salts. A characterization of granular phase change composites using the *T*-history method is published by Rady et al. [27]. There, it is concluded that the analysis of temperature variation along a cylindrical packed bed using phase changing granulates shows good agreement with the measured phase change characteristics. (More analyzed PCM by *T*-history are shown in Section 4.2, Table 3)

The main goal of this paper is to review the different techniques used to measure thermophysical properties of PCM available in the literature focusing on the original *T*-history method. In order to achieve the objective, first, previous methods designed for the same purpose and/or based on the same principle are exposed. Then, the original *T*-history method proposed and developed by Yinping et al. [23] is presented to underline its contributions. Finally, other scientific publications focused on improving the method are discussed and their contribution shown.

2. Thermal analysis methods for PCM

When choosing a PCM for a thermal storage system, suitable thermophysical, kinetic and chemical properties without overlooking economics and safety should be considered. Here, the aim is to focus on the thermophysical properties, which are the ones mainly needed to choose the suitable PCM for the storage equipment simulation and its design. Certain conditions should be fulfilled by the PCM [28,29]:

- (i) Melting temperature in the desired operating temperature range.
- (ii) High latent heat of fusion per unit volume so the required volume of the container to store a given amount of energy is smaller.
- (iii) High specific heat to provide additional significant sensible heat storage.
- (iv) High thermal conductivity of both solid and liquid phase to assist the charging and discharging energy of the storage system.
- (v) Small volume change on phase change transformation and small vapor pressure at operating temperature to reduce the containment problem.
- (vi) Congruent melting of the phase change material for a constant storage capacity of the material with each freezing/melting cycle.

Both thermal analysis (TA) and calorimetry techniques provide data which can be further evaluated in order to obtain the desired

thermophysical properties: phase change temperature (T_m) and enthalpy (H_m), and liquid and solid specific heats (C_p). TA differs from calorimetry since the former investigates the behavior of a sample as a function of temperature or time while calorimetry is based on recording the temperature, or heat of a sample when heating/cooling as a function of time. DSC is within these two concepts, as the output property is the heat flow as a function of both time and temperature. Here, it will be considered as a TA technique.

2.1. Conventional TA

The most common TA methods are listed in Table 1. The output property is specified for each technique [30]. Hemminger and Sarge suggested to distinguish between technique and method, as the method includes besides the evaluation and interpretation of the measured property [31,32]. Accordingly, both appear in abbreviation column.

Focusing on the commercial techniques (Table 1), the most used methods in PCM research community are DSC, DTA and, to a lesser extent, TGA. However, other techniques exist and are under development although they are not commercially available, as *T*-history. *T*-history first started as a calorimetry method [23], but Marín et al. [33] suggested a new data evaluation which shifted this method to the TA group (see Section 4.4).

2.2. Comparison on TA methods for PCM analysis

The choice of the suitable thermal analysis method for experimental data acquisition depends on the device outputs, measured values accuracy, experimental setup requirements as sample size, maintenance, the implementation, etc. As seen in Table 2, four different methods used for PCM characterization are compared taking into account relevant variables and outputs.

Sample size is an important characteristic to take into account when determining thermophysical properties. A small sample results in a decrease in the response time of the apparatus, and hence improvement of the temperature-resolution [34]. However, as PCM are mainly thought to be used in building applications [35], the larger the sample analyzed the more representative will be. Data obtained for small quantities on a laboratory scale may be misleading [36]. Also, [37] states that the *T*-history method has some advantages over other methods: it can be used, due to large sample size, for a wide variety of PCM (inorganic and organic, being encapsulated or composite), heating and cooling rates and temperatures ranges are variable and large enough to fit PCM for different applications. Therefore, for PCM characterization large samples are preferable. This could be achieved by the *T*-history method as shown in Table 2.

In the material characterization process, measurements and results evaluation are the most time consuming steps. Results evaluation time may be optimized with the experience of the researchers and when a protocol is well established. Measurement time depends only on the equipment selected for the analysis. Since more than one sample is usually analyzed for thermal stability [38] and repeatability purposes it is important to pay attention at the techniques that optimize measurement time. As shown in Table 2, *T*-history is the method with shorter experimental time.

Moreover, maintenance and equipment price are essential when choosing the method. The *T*-history method has the advantages of a simple experimental device as it can be built up with basic laboratory devices [39]. Again, as seen in Table 2, *T*-history is the method with lowest maintenance and lowest price.

DSC and DTA present similar features although the latter is mostly used for qualitative measurements. In particular, for enthalpy quantification the suitable techniques are DSC [40,41] and *T*-history.

Table 1
Common TA techniques with their related methods, abbreviation and the measured property.

TA measurement technique	Method	Abbreviation	Output property
Differential thermometry	Differential thermal analysis	DT/DTA	Temperature difference
Differential scanning calorimetry	–	DSC	Heat flow difference
Thermogravimetry	Thermogravimetric analysis	TG/TGA	Mass change
Themomechanometry	Thermomechanical analysis	TM/TMA	Deformation
Thermoacoustimetry	Thermoptometric analysis	TO/TOA	Optical properties
Exchanged/evolved gas measurement	Exchanged/evolved gas analysis	EGM/EGA	Gas exchange
Thermoelectrometry	Thermoelectrical analysis	TE/TEA	Electrical properties
Thermoacoustimetry	Thermoacoustimetric analysis	TO/TOA	Acoustic properties
Thermomanometry	Thermomanometric analysis		Pressure
Thermomagnetometry	Thermoagnetic analysis		Magnetic properties

Table 2
Comparison among four common TA methods.

	Thermogravimetric analysis (TGA)	Differential thermal analysis (DTA)	Differential scanning calorimetry (DSC)	*T*-history
Sample size (mg)	10–150	10–150	1–50	15,000
Measurement time (min)	100	100	100	40
Maintenance	++	++	++	+
Equipment price	++	++	++	+
Phenomenon	Thermal stability/decompositio, sublimination/evaportation/dehydration	Decompositio, glass transition, melting	Melting, glass transition, subcooling degree, reaction (curing/polymerization)	Melting, visual phase change, subcooling degree
Thermophysical properties	−%sample mass loss $f(T,t)$	$-\Delta T$ $f(T,t)$ $-H$ $f(T,t)$	$-Cp$ f(T,t) $-H$ $f(T,t)$ $-T_m$	$-Cp$ $f(T,t)$ $-H$ $f(T,t)$ $-T_m$ $-k$

T-history allows large samples analysis and entails less maintenance, equipment price and time evaluation than the other three presented. Thus, it is the most suitable method for PCM characterization. The major drawback is that the method presented here is not commercially available but can be assembled using standard laboratory components.

3. Previous methods

The basis of *T*-history method might lay on different previous methods. In this section a chronological overview among three non-commercial methods, that are based on the same principle, is exposed.

In particular, the following descriptions are focused in thermophysical properties measured by the device, its experimental setup and main components, the experimental procedure and, finally, the type of materials analyzed as well as some achieved results.

3.1. Vlasov et al. (1980)

The method proposed by Vlasov et al. [42] determines the following thermophysical properties during a change of state: thermal diffusivity in the liquid and solid phase, thermal conductivity in the liquid and solid phase and latent heat during the phase change. It consists in heating a solid sample until it is completely melt and record its inner temperatures when phase changing.

In Fig. 1(a), the heating of the sample is supplied by an electrical resistance (17) located at the top of the sample. So the sample (18) is heated from the top while its bottom and its sides are insulated (12). Therefore, when analyzing results, the heat transfer through the sample is treated as a one-dimension problem. The sample has cylindrical shape and it allows the correct recording of the seven thermocouples located into the sample (11).

The heating experimental procedure consists in three different periods as it can be seen in Fig. 1(b): (I) temperature homogenization inside the solid sample at $T < T_m$, (II) phase change and (III) temperature homogenization inside the liquid sample at $T > T_m$.

Although interesting results are obtained by the author, they are not validated with any other instrument or method.

3.2. Carré and Delaunay (1982)

The method designed by Carré and Delaunay [43,44] allows the simultaneous measurement of the thermal conductivity, the specific heat and the latent heat of PCM as well as of other complex fluids. The setup of this device is based in a guarded hot plate (Fig. 2(a)).

As it is shown in Fig. 2(a), the cylindrical cell containing the PCM sample is placed horizontally and the thickness-to-diameter ratio is small in order to avoid convective phenomena. The upper part of the sample is in contact with a brass plate with a resistance wire acting as the hot source (2). The bottom of the cell consists of a plate made of chromed brass in contact with the cold source refrigerated with water (5). In the lateral surface there is a material with a close thermal conductivity to the sample (7), ensuring a one-dimension heat transfer.

For sensing the temperature field in the phase-change material, an array of five-chromel-alumel thermocouples was stretches horizontally between a pair of parallel perforated insulating plates (14, 15 and 16). The measurement range is limited at 80 °C by errors introduced on the heat flux determination and also by the construction of the system. An example of temperature evolution given by the thermocouples in the sample is shown Fig. 2(b).

Thermophysical properties are measured in different regimes: (1) steady-state intervals to measure thermal conductivity, (2) transient regime between two stationary regimes to measure the variation of the specific heat versus temperature and (3) interval where the two phases coexist to measure latent heat of melting.

In order to validate results obtained by this instrument, thermal properties were first measured using DTA with a known material (a commercial wax).

3.3. Demirel and Paksoy (1993)

This method proposed by Demirel [45] tested the thermal performance of encapsulated heat storage materials in large non-stirred samples (samples that require slow heating process). It consists of measuring and comparing the energy loads of two identical thermostatic baths. The information provided by this method is: the heating and cooling curves, the enthalpy changes due to the sensible and latent heats, and also the heat transfer characteristics between the sample and the different working liquids.

Two identical baths Techne TU-16A (with a capacity of 42.5–48.5 l) are heated by an electrical resistance heater. The heating rates of the baths can be changed using a variac. One of the baths operates with encapsulated sample in Pyrex tubes of diameter 0.02 m and height of 0.30 m. The second bath operates with the working liquid (water, silicone oil or polyethylene glycol, depending on the operating temperature) under similar experimental

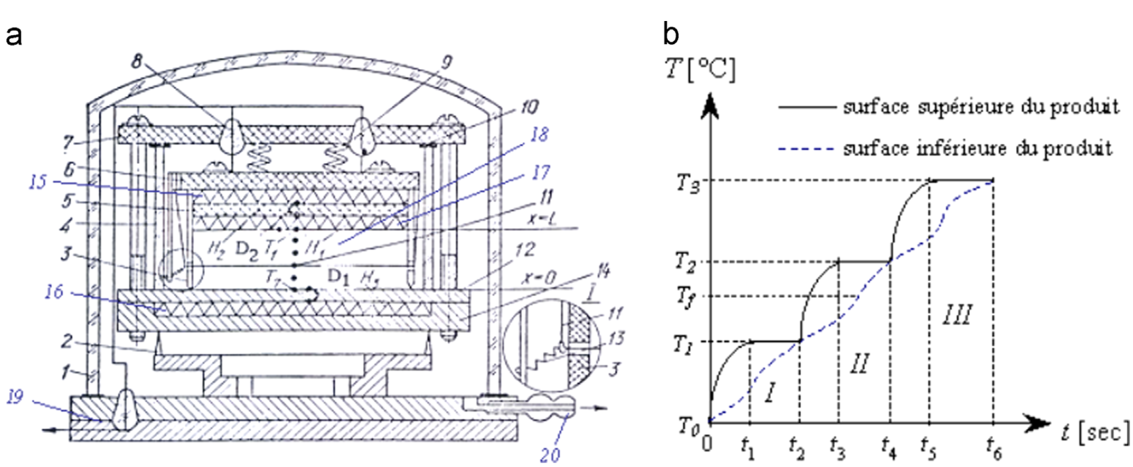


Fig. 1. (a) Automatic instrument proposed by Vlasov and Puchkov and (b) three-period heating [42].

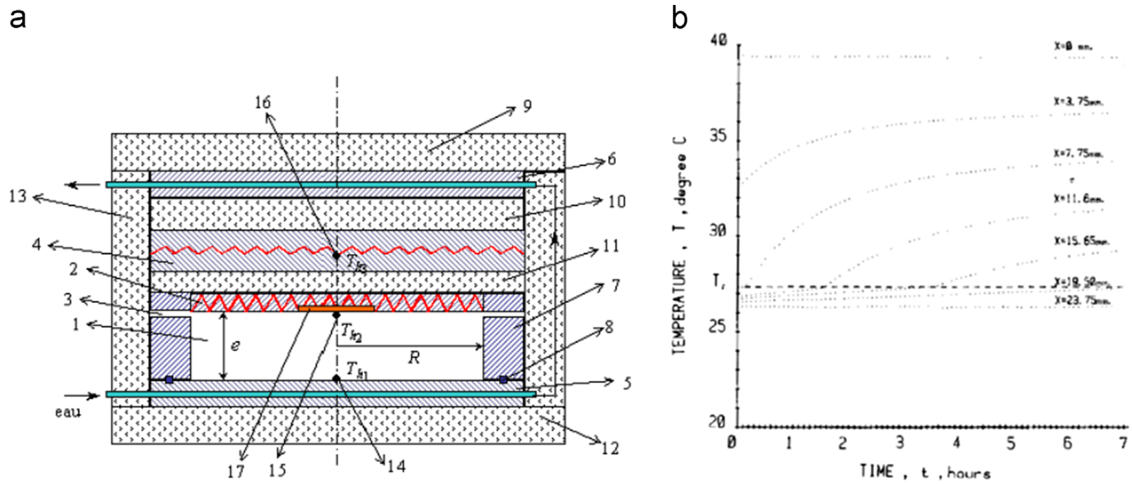


Fig. 2. (a) Experimental setup proposed by Carré and (b) resulting T versus t curves for $C_{18}H_{38}$ [43].

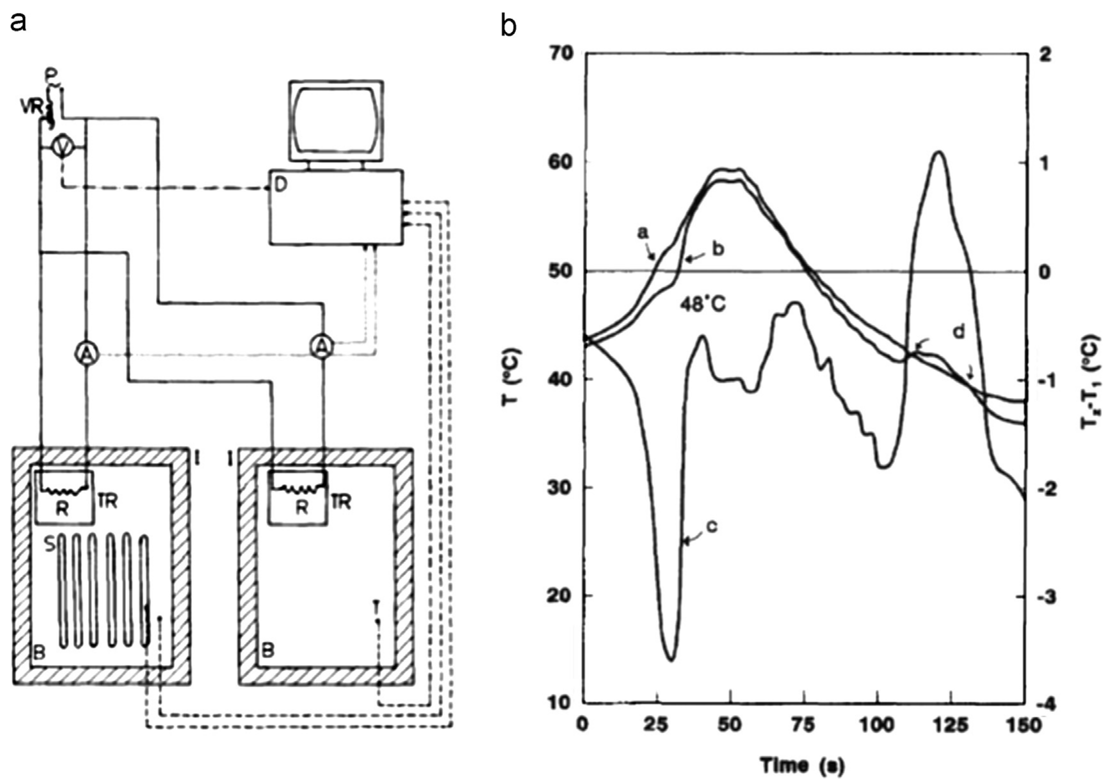


Fig. 3. (a) Twin bath test device and (b) heating and cooling curve for the zinc nitrate tetrahydrate.

conditions (Fig. 3(a)). The temperature sensors in the baths are platinum resistance thermometers (with an accuracy of ± 0.5 °C).

Assuming that the electrical energy input to the heating resistor is totally converted to heat, the power inputs of the baths are easily calculated. Two types of experiments have to be carried out to determine all the sample information: (1) only the working liquid in the second bath and both heated simultaneously and (2) a reference material with an identical encapsulation in the second bath.

This method is used in the range 0–200 °C. Materials tested are paraffin, high density polyethylene, ethylene glycol, brick and zinc nitrate tetrahydrate (whose T versus t curve can be seen in Fig. 3(b)). The approximate amount of sample is 1.7 kg, depending on the

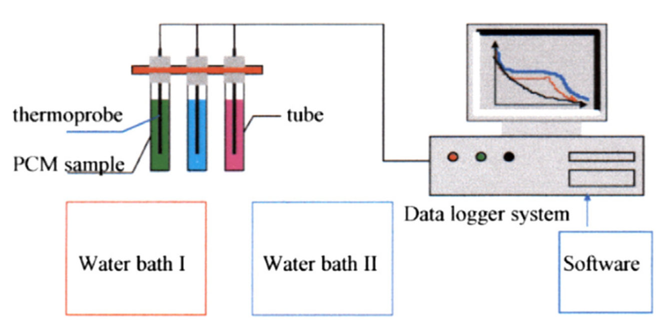


Fig. 4. First T-history setup proposed by Yinping et al. [23].

characteristics of the material. In order to validate results, a thermogram using DuPont 910 DSC was realized. The amount of energy and melting point match, but subcooling cannot be detected in DSC scale.

Three non-commercial devices have been presented. All of them record sample temperature as a function of the time and, consequently, allow determining thermal properties of a PCM sample. The main difference between them remains in the experimental setup: Vlasov et al. [42] and Carré and Delaunay [43,44] consider only the PCM sample in one chamber while Demirel and Paksoy [45] adds a reference material and another chamber to determine PCM thermal properties.

4. *T*-history method

4.1. Description of the original method

The *T*-history method was first developed by Yinping et al. in 1999 [23]. This method enables to obtain melting point, fusion heat, degree of subcooling, thermal conductivity and specific heat of several PCM samples simultaneously.

The abovementioned publication also provides:

- A description and a scheme of the experimental setup.
- The development of the mathematical model to calculate PCM properties, as Cp_l, Cp_s, H_m, with and without subcooling.
- The final results presentation (*T* versus *t*).
- The development of the equation to obtain the effective thermal conductivity.
- An error analysis.

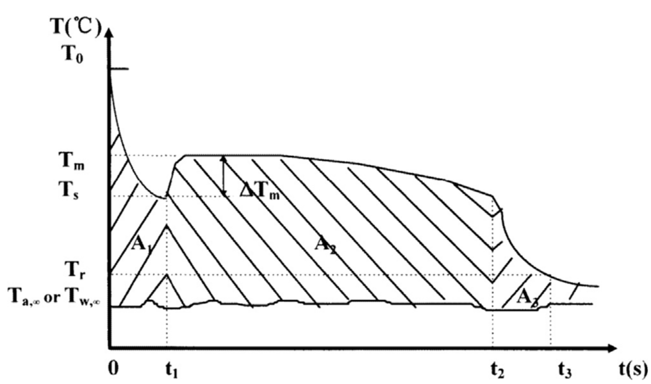


Fig. 5. Cooling temperature recorded versus time when PCM shows subcooling in the *T*-history method.

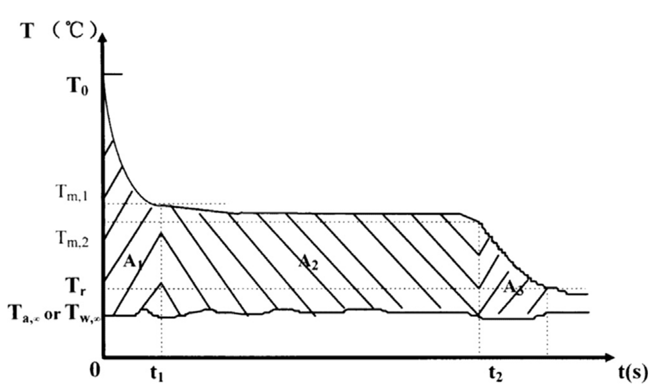


Fig. 6. Cooling temperature recorded versus time when PCM shows no subcooling in the *T*-history method.

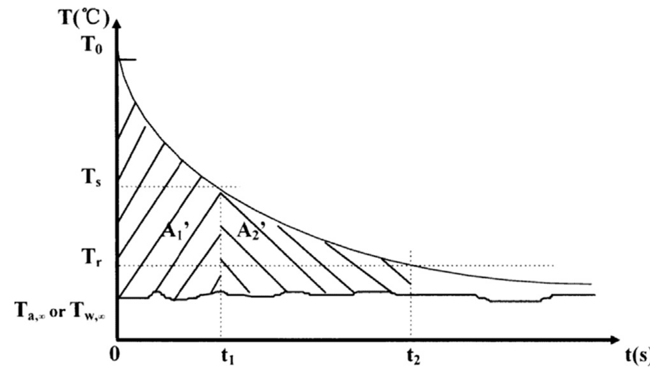


Fig. 7. Cooling temperature recorded versus time of the reference substance (water) in the *T*-history method.

The setup of the first *T*-history installation is shown in Fig. 4. Several test tubes are filled with PCM, one or more, and a reference, usually water, due to its well-known thermophysical properties. Accordingly, phase change process may be visually observed during the measurement.

Samples and reference material tubes are preheated in a water bath above the PCM melting temperature ($T_o > T_m$). Afterwards, they are simultaneously subjected to a sudden change of temperature, exposed to the ambient temperature T_∞. Their curves of thermal history (*T* versus. *t*) are recorded when cooling: Fig. 5 shows cooling process registered over time when PCM shows subcooling behavior (minimum peak between t_0 and t_1), Fig. 6 shows cooling process recorded over time when PCM subcooling is not observed, and Fig. 7 shows cooling process for reference substance (water in this experiment).

Thermal properties are determined when comparing PCM and reference curves. The heat transfer coefficient (*h*) is calculated following Eq. (1) and taking into account the reference *T* versus *t* recorded curve (Fig. 7). The well-known reference specific heat ($C_{p,w}$) is also considered. Plus, the experimental parameters: convective heat-transfer area (A_c), the test tube (m_t) and reference (m_w) masses and tube specific heat ($C_{p,t}$). Eq. (1) comes from balancing sensible heat released by the reference and convection heat transferred from the sample to ambient (Eq. (2)).

$$h = \frac{C_{p,w}m_w + C_{p,t}m_t}{A_c A_1'} \tag{1}$$

$$(m_t C_{p,t} + m_p C_{p,l})(T_o - T_s) = hA_c A_1 \tag{2}$$

where A_1' (see Fig. 7) is the integral of the temperature difference between the recorded reference temperature (*T*) and the ambient temperature (T_∞).

As the natural convective heat transfer coefficient is the same for all tubes, specific heat of PCM (C_p), for liquid and solid phase, and phase change enthalpy can be calculated from PCM energy balance.

$$m_p H_m = hA_c A_2 \tag{3}$$

$$(m_t C_{p,t} + m_p C_{p,s})(T_s - T_r) = hA_c A_3 \tag{4}$$

When a PCM shows subcooling (Fig. 5) the temperature range of phase change is between T_m and T_s. This difference is also called subcooling degree (ΔT_m).Whereas for PCM without subcooling, see Fig. 6, the range of phase-change is between $T_{m,1}$ and $T_{m,2}$. This difference is reflected in phase-change enthalpy determination.

Furthermore, an equation to calculate the effective thermal conductivity is developed for solid phase and analogously for liquid phase. Nevertheless, it can be only used for PCM which shows a clear interface between two phases when phase change

process occurs. The experimental part consists in suddenly expose the sample into a cool water bath. Convective heat transfer from the tube to the stirred cool water should be previously obtained by using the *T*-history curve of a tube containing mercury and the analogous form of Eq.(1) (replacing water subscript by mercury).

An error analysis in order to know the relative errors of each calculated thermophysical property is shown, which mainly come from the thermal sensors when measuring temperature.

Since first Yinping publication in 1999 [23], several research groups use his method and focus efforts on improving it. Some of them are working on the experimental setup, others in the mathematical model and/or results presentation. Neither thermal conductivity equation nor error analyzes are discussed among other publications.

4.2. Contributions on the experimental setup

The original experimental setup (Fig. 4) has been improved by Marín et al. [33,46], Sandness et al. [47], Lázaro et al. [48], Günther et al. [14] and Kravvaritis et al. [49].

Marín et al. [33] performed the cooling experiments in an insulate cool down chamber, showed in Fig. 8, instead of exposing the preheated tubes to the atmosphere. In this case less than 1 °C of temperature change, inside the chamber, during the experiment can be achieved and with negligible vertical temperature stratification. This idea to place the tubes during cooling process, in an insulated chamber was later adopted by Marín et al. [46], Lázaro et al. [48], Günter et al. [14,18] and Kravvaritis [49].

Marín et al. [46] proposed to place the tubes in horizontal position; this change diminishes the gravitational movements of the solid in the liquid. Results obtained with horizontal position adjust 15% better than the ones obtained with vertical position as it can be seen in Fig. 9. Horizontal tubes position was also suggested by Peck et al. [50].

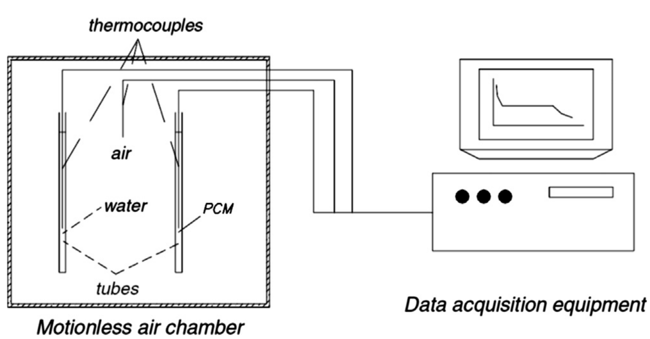


Fig. 8. Experimental setup proposed by Marín et al. [33].

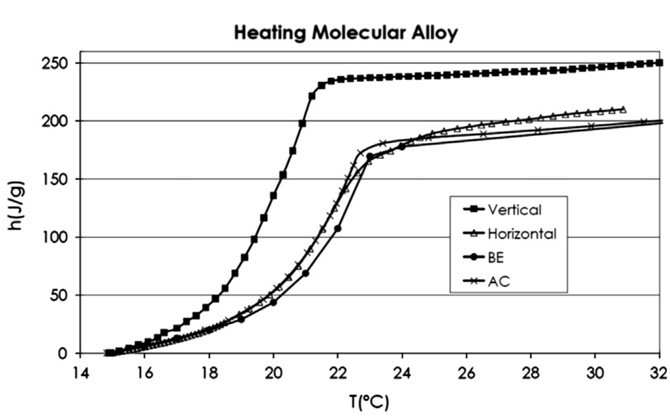


Fig. 9. Results comparison between vertical and horizontal *T*-history tubes position, energy balance (BE) and adiabatic calorimeter (AC) published by Marín et al. [46].

As seen in Yinping et al. [23], measurement errors in H_m, C_p and k mainly come from temperature measurement errors. To achieve a better accuracy of the thermophysical properties more precise instrumentation is required, therefore Marín et al. [46] implemented Pt-100 instead of thermocouples due to its higher precision, $\pm$0.05 °C with four threads assembly. Lázaro et al. [48] stressed the dependence of the results to sensors precision. Their suggestion is to proceed to a correct calibration of the sensors. Type *K* thermocouples were used in this study, being calibrated in a thermostatic bath using a calibrated Pt-100 as a reference and checking later by comparing the values when sample, reference and ambient are in thermal equilibrium before starting a measurement. Furthermore, Stankovic and Kyriacou [51] studied the *T*-history method concerning the adequate instrumentation and data acquisition system, details the environmental chamber and thermistors for the precise temperature control and sensing.

Marín et al. [46] covered the test tubes with aluminum foil in order to study the radiation effect. No significant differences were appreciated in the results with and without aluminum. So heat

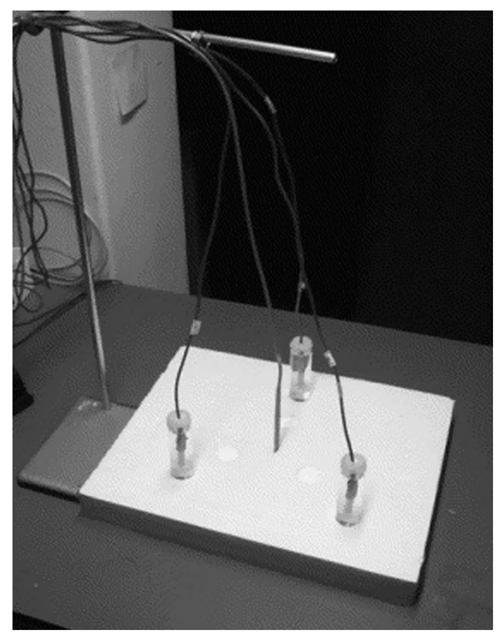


Fig. 10. Test tubes containing PCM in the experimental procedure of Sandnes and Rekstad [47].

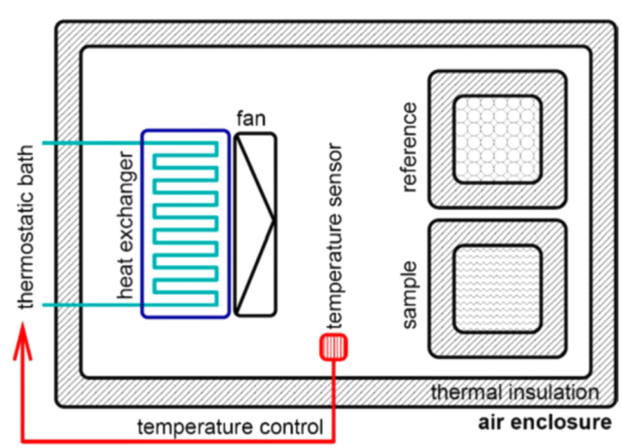


Fig. 11. Schematic drawing of *T*-history instrument as setup in ZAE Bayern (Germany) [48].

transfer by radiation is discarded, otherwise the mathematical model would have been modified.

The experimental procedure followed by Sandnes and Rekstad [47] differs from the others. Instead of running a reference tube with each single experiment, they determined the heat loss from the tubes as a function of temperature in a reference experiment performed in advance. The experimental setup suggested by Sandnes and Rekstad used tubes containing PCM, but no reference tube (Fig. 10). Therefore, they assumed that the heat loss is determined by the temperature difference to the surroundings alone (under equal conditions), and that is not necessary to evaluate heat loss as a function of time. This change in experimental setup and the corresponding assumptions have consequences to the mathematical model (see Section 4.3).

Marín et al. [46] detected internal gradients of temperature in the air enclosure and suggested to solve this problem by adding a proportional integral derivative (PID) control and dispersing the heat sources inside.

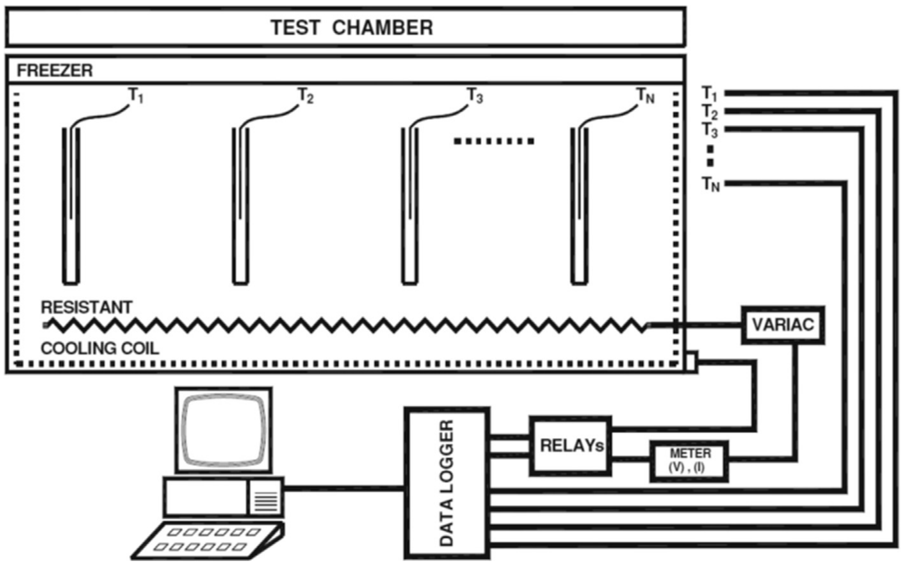


Fig. 12. *T*-history experimental setup [49].

Table 3
Different *T*-history installations with the corresponding analyzed PCM and controlled temperature range.

T-history Installation placement	PCM analyzed	References	Controlled temperature range
China, Tsinghua University	Capric acid, lauric acid, myristic acid, hexacosane, sodium acetate trihydrate, sodium thiosulfate pentahidrate, heptadecane, magnesium nitrate hexahidrate, salt hydrates mixtures	Yinping et al. [23]	Preheated samples above its melting point
Spain, Zaragoza University	Paraffin $C_{16}H_{34}$, molecular alloy of alkanes 34% $C_{16}H_{34}$ 66% $C_{18}H_{38}$	Marín et al. [33], and Lázaro [46]	Preheated samples above its melting point
Korea, Kyung Hee University	Sodium acetate trihydrate Paraffin $C_{22}H_{46}$, Lauric acid	Peck et al. [50] and Hong et al. [52,53]	Preheated samples above its melting point
Germany, ZAE Bayern	RT27, TH29, Ga, Hexadecane, Sodium acetate trihydrate+graphite	Günter et al. [14,18 and Lázaro et al. [48]	−20 °C to 65 °C [48], −5 °C to 80 [14,18]
Norway, Oslo University	Disodium hydrogen phosphate dodecahydrate, sodium acetate trihydrate, commercial STL-47	Sandness and Rekstad [47]	Preheated samples above its melting point
Greece, Heroon Polytheniou	Greek market paraffin, Ethyl alcohol, RT20, RT27, RT58 and SP 25A8	Kravvaritis et al. [49,54]	−30 °C to 120 °C
United Kingdom, City University London	RT21	Stankovic and Kyriacou [51]	−10 °C to 100 °C

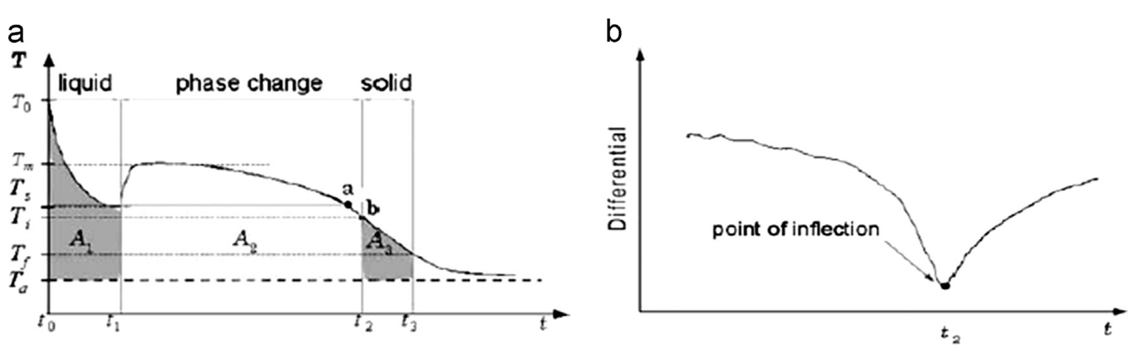


Fig. 13. Hong et al. 2003 proposal [52]; (a) *T* versus *t* recorded curve and (b) first derivative of the curve *T* versus t to detect the boundary (t_2) of phase change.

Günther et al. [14] and Lázaro et al. [48] designed a new installation at ZAE-Bayern (Germany), see Fig. 11, consisting in a PID controller connected to a thermostatic bath, which can provide a temperature range from −20 °C to 65 °C and hold repeated measurements. Kravvaritis et al. [49] also adopted this incorporation in their equipment. Only Lázaro et al. [48] and Kravvaritis et al. [49] setup the test chamber in order to allow measurements upon heating and cooling and to automate the system. Inside the air enclosure, the sample and the reference are insulated, being the insulation the predominant part of the total heat resistance. So the heat transfer coefficient from the ambient to the sample and reference can be considered the same [48].

On the other hand, Kravvaritis et al. [49] decided to place electric resistances and cooling coils, see Fig. 12, achieving a wider range of temperatures from −30 °C to 120 °C (double distilled water (WFI) was used as the reference fluid).

Since the original *T*-history setup was presented, many researchers have been working on improving it. Table 3 summarizes each existing setup, with the analyzed PCM and temperature range that the built equipment can achieve, ordered in time.

4.3. Contributions to the mathematical model

The original mathematical model and data evaluation have been widely modified but in a disperse way. Hong et al. [52], Marín et al. [33], Sandness et al. [47],and Kravvaritis et al. [49] have contribute in improving the mathematical model, mainly in order to increase method's accuracy.

First contribution, Hong et al. [52], includes three factors and therefore, modifies original equations for specific heat and heat of fusion. First, the boundary t_2 (see Fig. 13) between latent heat and solid sensible heat range is redefined, when PCM shows subcooling. This can be detected by representing the first derivative of the curve T versus t, being the inflection point the wanted boundary between phase change and solid state periods. Secondly, they also include sensible heat of tubes and PCM when calculating the heat of fusion. Last suggestion is to use tube mass contacting with the PCM or water instead of total tube mass. Results for sodium acetate trihydrate are shown taking into account all these factors. Further publication of the same author [53], gives more results for two PCM: paraffin $C_{22}H_{46}$ and Lauric acid. These suggested factors have never been adopted by other researchers, except the idea of taking into account the specific heat released by the test tube during phase change [33,47].

The second improvement, Marín et al. [33], was focused on achieving temperature dependent properties in order to properly select a heat storage material. Instead of thinking on the variation of the temperature with time, in Marín et al. [33] is suggested to use enthalpy–temperature curves. These authors based their improvement on modifying the original mathematical model, hence varying the temperature over very small intervals, ΔT_i, corresponding to time intervals $\Delta t_i = t_{i+1} - t_i$. Moreover, they also suggest including sensible heat of the tube when calculating phase change enthalpy. Therefore, the original equation Eq. (5) becomes Eq. (6) where T_i is the average temperature in the interval, regarding Figs. 6 and 7 and Eq. (3).

$$H_m = \frac{m_w C_{p,w} + m_t C_{p,t}}{m_t} \frac{A_2}{A_1'} (T_o - T_s) \tag{5}$$

$$\Delta H_p(T_i) = \left(\frac{m_w C_{p,w}(T_i) + m_t C_{p,t}(T_i)}{m_p} \right) \frac{A_i}{A_i'} \Delta T_i - \frac{m_t}{m_p} C_{p,t}(T_i) \Delta T_i \tag{6}$$

Nevertheless, enthalpy–temperature curves are more useful in PCM research field and can be determined as the sum of the enthalpy intervals, assuming a constant value of $H_{p,o}$ as a reference

$$H_p(T) = \sum_{i=1}^{N} \Delta H_{p,i} + H_{p,o} \tag{7}$$

From Eq. (7) phase change temperature and enthalpy can then be calculated. Specific heat values, liquid and solid, can be obtained by computing the suitable slope of the curve at the selected temperature, as shown in Eq. (8)

$$C_p = \frac{\delta H}{\delta T} \tag{8}$$

Sandness and Rekstad [47], as aforementioned (Section 4.2), purpose another set of equations to describe enthalpy–temperature curves. Their final results follow Marín et al. [33] suggestion (Eqs. (7) and (8)) notwithstanding that the development of the equations is differently set up. Hence, the heat loss from the reference tube (q_i) is given by the reference material, water, the test tube and the temperature sensor

$$q_i = (m_w C_{p,w} + m_t C_{p,t} + m_{sn} C_{p,sn}) \frac{\Delta T_{w,i}}{\Delta t_i} \tag{9}$$

When representing heat loss, determined by Eq. (9), as a function of temperature difference between reference sample and ambient, data can be fitted to a second degree polynomial

$$q_{(T_{ref} - T_{amb})} = c_1 (T_w - T_\infty) + c_2 (T_w - T_\infty)^2 \tag{10}$$

Then, once the heat loss coefficients (c_1 and c_2) are known, the heat loss from each PCM tube at a particular time interval (q_i) can be calculated as follow:

$$q_i = c_1 (T_{p,i} - T_{\infty,i}) + c_2 (T_{p,i} - T_{\infty,i})^2 \tag{11}$$

The heat loss from the PCM alone in the time interval is determined by subtracting the specific heat released by the test

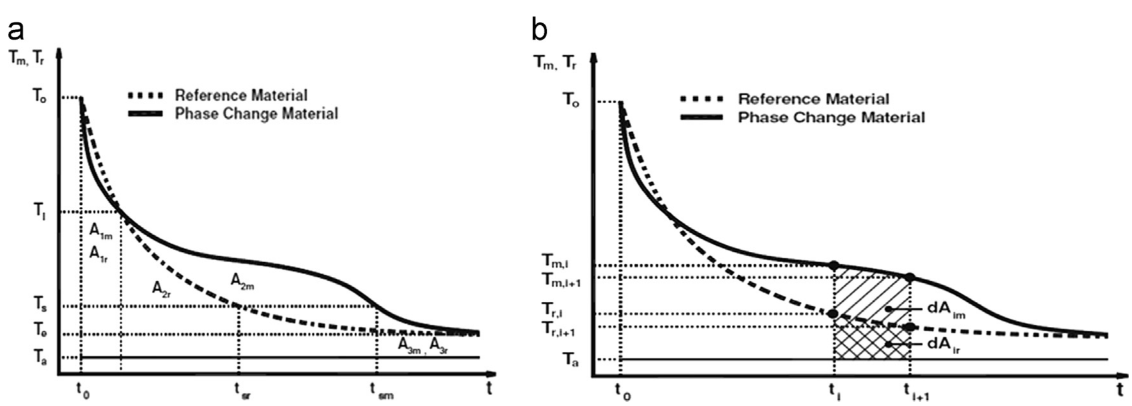


Fig. 14. Cooling curves of PCM and reference fluid, according to (a) original method [23] and (b) Kravvaritis et al. [49].

tube itself and the temperature sensor from the total heat loss

$$q_{p,i} = q_i - (m_t C_{p,t} + m_{sn} C_{p,sn}) \left(-\frac{\Delta T_{p,i}}{\Delta t_i} \right) \quad (12)$$

The enthalpy change in the interval, for the PCM, can then be determined as

$$\Delta H_i(T_{p,i}) = \frac{q_{p,i} \Delta t_i}{m_p} \quad (13)$$

Finally, to get the cumulative enthalpy as a function of temperature Eq. (7) is used. Eq. (8) is used for the specific heat.

Sandness and Rekstad [47] pointed out that the dominating source of measurement error originates from the simplified assumptions that are made for the heat transfer processes, given by the geometry and material properties setup. Since the setup of the original method [23] was modeled as a lumped capacitance model [54], this model can only be applied when Biot number is < 0.1, assuming that temperature does not vary with position but with time. Regardin Biot equation, if h (convective heat transfer coefficient of air outside a tube) is 5–6 K m^{-2} K^{-1} the condition of Bi < 0.1 can be satisfied when $k_s > 0.2$ W m^{-1} K^{-1}, otherwise the mathematical model should be redeveloped. Several PCM do not satisfy this condition [55]. In addition, in [47] there is an estimation of the error associated in enthalpy results due to the sample uniform temperature assumption.

Another contribution in measurement processing was published by Kravvaritis et al. [49]. Their proposal is based on the use of thermal delay (temperature difference) between PCM and a reference fluid at any specified time. The original method [23] considered time delay at any specified temperature, as shown in Fig. 14. This leads to an increase of accuracy and to a reduction of time processing. The same authors provide further experimental measurements using ethyl alcohol and double distilled water as reference fluids [56].

The modified *T*-history in his derivative version, also called d*T*-history, was presented by Moreno-Alvarez et al. [57]. Their objective is to achieve thermodynamic consistency with phase transitions theory, by including the important experimental effect of the speed of the thermal process in calorimetric calculations. They also base the differential formulation of the method on the same fundamental suppositions of the technique (Bi < 0.1 and equality of the convective heat transfer coefficients). The starting point equation (Eq. (14)) is the energy balance for the heat flow:

$$\frac{dT}{dt} = \dot{T} = -h \frac{A(T - T_\infty)}{C_p m} \quad (14)$$

By this way, results presented in [47] show the effect of different cooling rates in measurements for the same material which is of importance due to the dependency of subcooling effect on the heating rate. Nonetheless, *T*-history curves must be used carefully, since they present some limitations, such as an extreme sensibility to rapid changes in temperature gradients between samples and ambient.

4.4. Contributions on the results presentation

Traditionally, *T*-history results are presented in figures. Sample, reference, and ambient temperature are plotted versus time (see Figs. 5–7). However, results format presentation has been mainly rearranged by Marín et al. [33] whose purpose was based on showing enthalpy versus temperature instead of temperature versus time (Fig. 15). This can be understood as a consequence of their modification suggested on the mathematical model.

This improvement has been also adopted by Lázaro et al. [48] and by Sandness and Rekstad [47], the last one specifically for subcooling salt hydrates. Sandness and Rekstad [47] assure that this type of plots provide direct visualization of important thermophysical properties for thermal energy storage applications. Nevertheless, Sandness and Rekstad [47] differs from Lázaro et al. [48] in the experimental procedure (as seen in Section 4.2).

Kravvaritis et al. [49] supply an expression for the effective PCM thermal capacity (C_{peff}) as it can be seen in Fig. 16. This function contains much more information than the final results given by the original method. It provides the effective specific heat as a function of temperature which is needed for simulation instead of an average value for solid and for liquid.

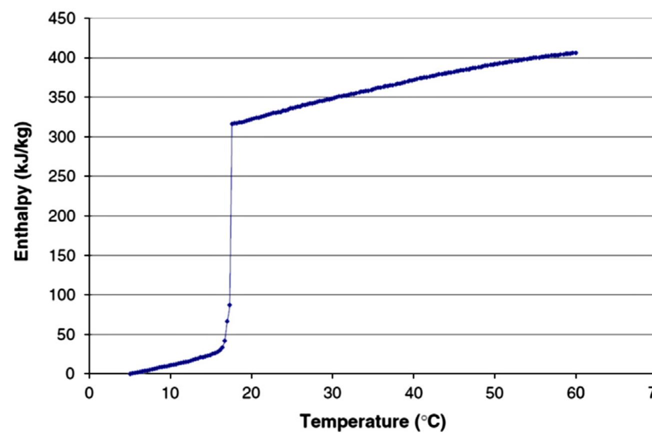


Fig. 15. Enthalpy–temperature curve obtained from experimental data [33].

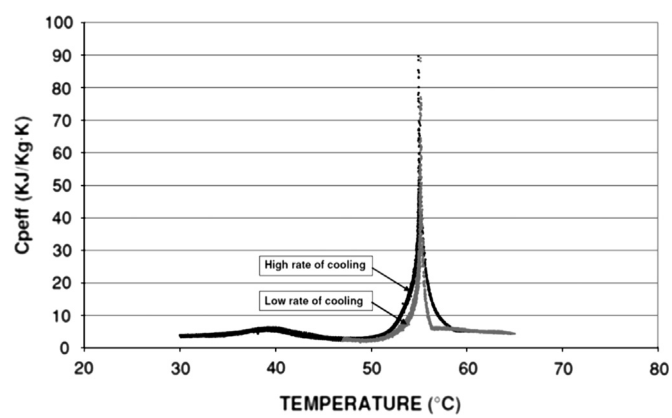


Fig. 16. Effective thermal capacity in terms of the temperature [49].

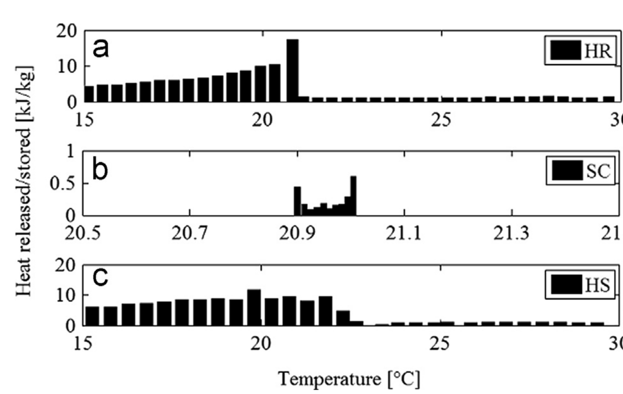


Fig. 17. Experimental results for the heat storage in the given temperature intervals for the RT21 PCM (m=41 g). (a) Heat released (HR) upon sample freezing, (b) degree of Subcooling (SC) upon sample freezing, and (c) heat stored (HS) upon sample melting [51].

A standard on how to present the PCM data is described in Mehling et al. [58]. This standard eliminates the ambiguities that arise from only giving melting point and latent heat data and has been adopted when presenting *T*-history results by Stankovic and Kyriacou [51] as can be seen in Fig. 17.

5. Conclusions

The *T*-history method presents several advantages when compared to the commercially available thermal analysis methods (DSC, DTA) to determine PCM thermophysical properties. The most significant are large sample amount, optimized measuring time and a simple and economical built up.

Since 1999, when the original *T*-history was presented, several contributions have been published in order to improve this method. In this paper all these suggestions were reviewed and gathered in three big groups regarding the experimental setup, the mathematical model and the final results presentation. Authors working on *T*-history have reached important improvements as higher results accuracy, to adapt the model to obtain the thermophysical properties as a function of temperature, to automatize the technique, make possible to perform also cooling experiments, etc. Moreover, new challenges have arisen as enhancing instrumentation and data acquisition system, to widen the chamber temperature range to fit more PCM applications, to minimize sample internal gradients, etc.

In PCM research community there is a lack of one TA method convenient to measure larger PCM samples. *T*-history is the suitable candidate. To move towards a commercial and available one is important to get in consensus among all researchers to suggest a common instrumental setup, data analysis and presentation of final results.

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